Recent Application of Neutron Activation Analysis to Coal

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The possibility of environmental contamination resulting from current and proposed uses of large quantities of coal for combustion, liquefaction, and gasification has been discussed extensively. In order to evaluate the potential for harm, many studies have been undertaken to determine the trace-element compositions of various coals and the elemental budgets of coal-consuming facilities, such as power plants. Neutron-activation analysis has been used extensively for these studies, because the method has good sensitivity for a large number of elements of interest, is nondestructive, and, when automated, can be used to process samples rapidly and efficiently.

In common with other analysts, the activation analyst strives to reduce interferences and determine the elements of interest. The methods used to discriminate among the large numbers of radioactive nuclides produced by neutron bombardment are listed in Table 1. Such an outline is useful for a general discussion of neutron-activation analysis, but variations of the techniques may deviate from this table. Because of the large numbers of coal samples that must be analyzed, instrumental techniques have been employed whenever possible to avoid time-consuming radiochemical separations and the possibility of loss of volatile elements.

Although all of the techniques in Table 1 are instrumental, with the exception of radiochemical neutron-activation analysis (RNAA), the term instrumental neutron-activation analysis (INAA) is ordinarily reserved for the method in which gamma-spectra are collected using high-resolution gamma-detectors (lithium-drifted germanium or intrinsic germanium) at different decay times following neutron bombardment of the sample. This technique allows the determination of as many as 40 elements in coal and fly ash, and many such multi-element procedures have been reported (1-10). The elements determined include Al, As, Au, Ba, Cr, Ca, Ce, Cl, Co, Cr, Cs, Cu, Dy, Eu, Fe, Ga, Hf, I, K, La, Lu, Mg, Mn, Na, Nd, Ni, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Ti, U, V, Yb, and Zn. However, about seven of these elements (Au, Ba, Ga, Ni, Rb, Ti, and Zn) exist in some coal at concentrations near their limits of detection, and, therefore, the exact number of elements that can be determined depends on the composition of the individual coal sample. The U.S. Geological Survey used INAA to determine many of the elements listed above in eighteen coal samples from various locations in the United States (11) and, more recently, as one of the analytical techniques for routine analysis of 2,000 Eastern U.S. coal samples. However, special emphasis is placed on determining As, Cr, Co, Sb, and Se, because these elements are more difficult to determine by other analytical techniques.

If a sample is surrounded with Cd during neutron bombardment, then activation by epithermal neutrons is enhanced relative to that by thermal neutrons and some selectivity may be achieved. This technique has been used to determine U and Th in coal and coal ash (12, 13). At the U.S. Geological Survey, Rowe and Steinnes made an extensive study of the activation analysis of coal and fly ash that included a comprehensive comparison of thermal and epithermal INAA (10). They found that the sensitivities for Ba, Cs, Ga, Hf, Ho, In, Mo, Ni, Rb, Sb, Se, Sr, Ta, Tb, Th, U, W, and Zr were improved when epithermal INAA was employed.

Fast neutrons (14 MeV) from a neutron generator may be used to activate light elements. O, N, F, Si, and Al have been determined in coal by this rapid and routine technique (14-17). Because the distribution of O between the organic and mineral components of coal is highly variable and because the other elements are determined by other routine techniques, the fast neutron method is seldom used in coal analysis.

Prompt gamma-counting (PG) involves detecting the gammas emitted immediately after neutrons are absorbed during bombardment. This method has been used to determine Fe, B, and Cd in coal (18, 19).

The delayed-neutron counting technique (DN) is used (20) primarily to determine U and Th. One-minute neutron irradiations are followed by several minutes of counting the neutrons emitted by the fission-daughters of U and Th. Thermal and epithermal neutron irradiations are performed to differentiate between U and Th. At the U.S. Geological Survey, we use automated neutron counters to analyze about 7,000 samples per year by this technique (11, 21). Using 5-g coal samples, the carbon matrix causes neutron thermalization within the sample, so it is important to prepare standards by spiking a suitable coal with U and Th. We maintain good accuracy by intercalibration with isotope dilution-mass spectrometric U and Th standards.

Uranium may also be determined by fission-track (FT) counting (22). This technique is very useful for small samples (<100 mg), such as mineral separates. We have automated this procedure by using spark-counting or more recently, by employing an image analyzer. Fission-track maps of pellets prepared from coal powders indicate whether the U is distributed evenly in the organic matrix or is concentrated in discrete mineral phases such as apatite. Maps of thin sections of coal can be used to find minerals containing high concentrations of U, and these minerals may then be identified by suitable techniques such as electron-microprobe analysis.

Radiochemical neutron-activation analysis (RNAA), in which radiochemical separations are performed after neutron irradiation and prior to counting, has been used to determine As, Br, Cd, Cs, Hg, Ga, Rb, Sb, Se, U, and Zn in coal (23, 24). However, in recent years these methods have been replaced to a great extent by the faster and less tedious instrumental techniques discussed above. RNAA still is used for several elements (e.g., Hg and Cu) for which instrumental methods are not sufficiently sensitive (6, 25), and to calibrate standard materials when the highest levels of precision and accuracy are required.

Table 1. Methods of discrimination employed in various neutron-activation analysis techniques

INAA = Instrumental Neutron Activation Analysis
FNAA = Fast Neutron-Activation Analysis
PG = Prompt Gamma-Counting
DN = Delayed Neutron Counting
FT = Fission Track
RNAA = Radiochemical Neutron-Activation Analysis

	NAA Technique						
	INAA						
Method of Discrimination	Thermal	Epithermal	FNAA	PG	DN	FT	RNAA
Energy of bombarding neutrons:							
thermal (0.1 eV)	X			X	X	X	X
epithermal and resonance (0.1-1000 eV)		X			X		X
fast (14 MeV)			X				
Irradiation time	X	X	X		X		X
Decay time after irradiation	X	X	X		X		X
Emitted particle measured:							
gamma (spectrometry)	X	X	X	X			X
neutron					X		
fission fragment						X	
Chemical properties							X

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